

Brazilian oils and butters: the effect of different fatty acid chain composition on human hair physiochemical properties.

Hair cosmetics are an important tool that helps to increase patient's adherence to alopecia and scalp treatments. This article reviews the formulations and the mode of action of hair cosmetics: Shampoos, conditioners, hair straightening products, hair dyes and henna; regarding their prescription and safetiness. The dermatologist's knowledge of hair care products, their use, and their possible side effects can extend to an understanding of cosmetic resources and help dermatologists to better treat hair and scalp conditions according to the diversity of hair types and ethnicity. One of the potential benefits of such formulations is to avoid hair restoration treatments as recommended by <https://www.bahrs.co.uk/> and practiced at clinics such as EA Clinic at <https://www.eaclinic.co.uk/treatments/fue-hair-transplant/>

Keywords: Hair, hair care, hair cosmetics

Introduction

Although dermatologists are experts in managing scalp and hair diseases, the esthetic of some cosmetic therapies still remain elusive. Knowledge of hair cosmetics and esthetic procedures as well as of the hair shaft structure and physical behavior is indeed relevant in today's medical practice.^[1] Although hair cosmetics are widely available, the medical literature is rather scarce, and specialized literature is not readily accessible. The aim of this chapter is to allow a better understanding of the hair shaft structure and behavior, as well as information about the hair cosmetics. Knowing their mode of action, safetiness and ingredients will enable the physician to better assess different problems secondary to cosmetic treatments. Cosmetic hair care procedures are mostly used by African-descendent women, whose hair fragility has been related to be worsen by hair care practices. According to McMichael^[2] hair fragility leading to breakage can occur due to genetic predisposition, weathering from various hair care practices. Hispanic patients also have curly or very curly hair that may clinically behave as sensitive as African hair when exposed to hair care procedures. Although scientific data is lacking to prove whether Hispanic hair is really as sensitive, it is common to see Hispanic women with chemically straightened hair, suffering from hair breakage and asking for the dermatologist help and advice to overcome the problem. Also, it is important to distinguish hair shed due to telogen effluvium from hair shed due to hair shaft breakage, which is not always clear from the patient point of view.

Hair

Hair is an integrated system with a peculiar chemical and physical behavior. It is a complex structure of several morphological components that act as a unit. The hair shaft of mammals is divided into three main regions: Cuticle, cortex and medulla. The medulla is present in coarser hair like grey hair, thick hair and beard hair, and it is absent in fine hair of children. There is more medulla in the coarser hair of Asians than Caucasians. The medulla may be involved in the splitting of hairs since it provides an area of weakness as a pathway for the propagation of cracks along the axis of the fiber.^{[3],[4]}

The cuticle is a chemically resistant region and consists of flap overlapping scales (keratinocytes) like shingles on the roof. The shape and orientation of the cuticle cells are responsible for the differential friction effect in hair. The cuticle is generally formed by 6-8 scales thick for Asians, slightly less in Caucasians and even less in African hair. A thinner cuticle layer makes African hair more prone to breakage. Each cuticle cell contains a thin proteinaceous membrane, the epicuticle, covered with a lipid layer that includes the 18-methyl eicosanoic acid (18-MEA) and free lipids. Beneath the cuticle cells membranes there are three layers, all containing heavily cross-linked protein, mostly cystine, the A-layer, the exocuticle or B-layer and the endocuticle. The first one contains the higher amount of cystine, and the third one contains the lowest. The 18-MEA is responsible for the hydrophobicity of the hair and its removal by alkaline chemical cosmetics procedures may damage hair by increasing hydrophilia.^[5]

The cell membrane complex (CMC) is intercellular matter. CMC consists of cell membranes and adhesive material (cement) binding the cell membranes between two cuticle cells, two cortical cells and cuticle-cortex cells. The most important layer of the CMC is called the beta-layer, and it is considered to be the intercellular cement and it is sandwiched by other layers from each cell. The CMC and the endocuticle are very vulnerable regions to the chemical treatments such as bleaching, dyeing and hair straightening/perm procedures. Also, the everyday

grooming and shampooing friction may disrupt the CMC. ^{[3]:[4]:[5]}

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CMC fractures may be seen before the hair fiber is ruptured. The exposure to repeated rough washing, unprotected drying, friction actions, sunlight and alkaline chemical treatments lead to a decrease in the lipid content of the cell surface changing it from the state of hydrophobicity to a more hydrophilic, negatively charged surface. ^{[3]:[4]:[5]:[6]}

The cortex constitutes the major part of the mass of the human hair, and it is formed by elongated, fusiform cells connected by a CMC and contains protein and melanin granules. The cortex cell also contains spindle-shaped fibrous structures called macrofibrils, each one consists of microfibrils that are highly organized fibrillar units and matrix. The matrix is formed by crystalline protein of high cystine content. The macrofibrils are arranged in a spiral formation. Inside the microfibrils there are subfilamentous units called protofilaments, each contains short sections of alpha-helical proteins in coiled coil formation polypeptide chains of proteins. The alpha-helix is held coiled by chemical forces such as: Ionic forces, hydrogen bonds, Van de Waal forces and disulfide bonds. Hair straightening process consists on breaking the forces that hold the coil, allowing it to be stretched. If the rupture of the chemical bonds is followed by curling the hair, it is called "perm," meaning permanent curling. The process of reduction the hair involves hair swelling and very alkaline substances such as sodium or lithium hydroxide, guanidine, ammonium thioglycolate, pH higher than 9.0. All this can produce splits or cracks to the endocuticle and the CMC, but the major damage to hair after using hair reducing products is indeed due to misuse of the products and lack of care during combing hair in the reduced state. ^{[4]:[5]:[6]:[7]} Hair damage caused by the use of chemical procedures can be minimized, avoided or repaired by the correct use of hair care products. Hair cosmetics may enhance hair hydrophobicity, strengthen the cuticle and minimize electrical charges and friction forces. ^{[2]:[5]:[6]:[8]}

Hair damage



The hydrophobicity of the hair is possible thanks to the 18-MEA lipid layer. Removal of this covalently linked fatty acid renders the fiber hydrophilic. When wet, virgin hair can be stretched by 30% of their original length without damage; however, irreversible changes occur when hair is stretched between 30% and 70%. Stretching to 80% causes fracture. ^[4] Hair is porous and damaged hair is intensely so. Water absorption causes the hair shaft swelling. Excessive or repeated chemical treatment, grooming habits, and environmental exposure produce changes in hair texture and if extreme can result in hair breakage. These changes can be seen microscopically as "weathering" of the hair shaft and contribute to tangling, and frizzing. Weathering is the progressive degeneration from the root to the tip of the hair. Normal weathering is due to daily grooming practices. When the hair is extremely weathered and chemically treated, there may be scaling of the cuticle layers, removal of the 18-MEA and cuticle crack. If the cuticle is removed, the exposure of the cortex and further cortex damage may lead to hair fiber fracture. The use of hair cosmetics may restore hair cuticle damage and prevent hair breakage by reducing friction and water pick up. ^{[2]:[4]:[5]:[8]:[9]}

Shampoos



Shampoos are not only scalp cleaners, but indubitably act as preventing the hair shaft damage. Many scalp diseases are also treated by active ingredients that are added to the shampoo's formulations. It is desirable that whatever may the disease or condition be (dermatitis, seborrhea, alopecia, psoriasis), the hair strands are kept aesthetically presentable, preserving its softness, combability and shine while treating the scalp. ^{[10]:[11]:[12]:[13]:[14]:[15]}

Shampoos are typically composed of 10-30 ingredients although products with as few as four ingredients are available. The products are grouped into: (1) Cleansing agents; (2) additives that contribute to the stability and comfort of the product; (3) conditioning agents, intended to impart softness and gloss, to reduce flyaway and to enhance disentangling facility, and (4) special care ingredients, designated to treat specific problems, such as dandruff and greasy hair. ^{[11]:[12]:[13]}

Conditions that are mostly affected by the use of aggressive shampoos are: Difficulty in untangling the strands, and the frizz effect. Attrition, the main cause of frizz, can be minimized by adequate formulation of cleaning products. On the other hand, if the shampoo formulas do not present the adequate composition, fiber attrition is aggravated. ^{[10]:[16]}

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Although considered as safe products, shampoos can cause contact dermatitis. Common allergens in shampoos are: Cocamidopropyl betaine, methylchloroisothiazolinone, formaldehyde-releasing preservatives, propylene glycol, Vitamin E (tocopherol), parabens and benzophenones. ^{[14]:[15]}

Surfactants



Surfactants are cleaning agents that substituted soap ^[Table 1]. They act through the weakening of the physicochemical adherence forces that bind impurities and residues to the hair. Surfactants dissolve these impurities, preventing them from binding to the shaft or the scalp. The cleansing ability of a shampoo depends on how well it removes grease as well as the type and amount of surfactants used. ^{[5]:[10]}

Residues are nonsoluble fats (sebum) that do not dissolve with water. In order to be removed from the hair shaft, surfactants present a hydrophobic molecular portion, and another hydrophilic. The former will chemically bond with the fat, while the latter will bond with the water. The surfactants are generally composed of a chain of fatty hydrocarbons (tail) and a polar head. The polar extremity is capable of giving this portion of the molecule hydrophilic traits that allow it to dissolve in water and wash away the residues. The surfactants in contact with the water attain the structural formation of a micelle. Their structure becomes spherical with a hydrophilic exterior, which can be rinsed with water, and a hydrophobic interior where the fats and residues are binded. When enough shampoo molecules have embedded their hydrocarbon ends in the particle, the surrounding water molecules attract the ionic ends of the surfactant. The particle then becomes emulsified, or suspended in water. In this form, it can be rinsed away. ^{[4]:[5]:[11]:[12]:[13]} Depending upon the electric charge of the polar extremity, the surfactants are classified in four groups: Anionic, cationic, amphoteric and nonionic. The main cleansing agents are anionic. The soap, which is also an anionic detergent, in contact with water, leaves an alkaline residue that is very harmful to the hair and skin and that precipitates in the form of calcium salts which accumulate in the hair strands, leaving them opaque and tangled. Such effects do not happen with the new anionic surfactants that are derived from the sulfation of fatty acids and analogue polioxiethylenes (alkyl sulfates, alkyl ether sulfates) which are smooth cleansers and cosmetically superior. The current expression "sulfateless shampoo" refers to a preparation without the anionic surfactant. Theoretically the sulfateless shampoo creates a minimum electrical net, but there are no published analysis about effectiveness of these products regarding either cleansing power or hair shaft aggression. ^{[11]:[12]:[14]:[15]:[16]}

Cationic, amphoteric and nonionic surfactants are added to some shampoo formulas to reduce the static electricity generating effects caused by the anionic surfactants. Since they carry a positive charge, cationic surfactants bond quickly to the strands negatively charged due to the use of anionic surfactants and reduce the frizz effect. Besides, they optimize the formation of foam and the viscosity of the final product. The static electricity verified after the use of shampoo is exactly the result of a balancing out between the electric charges during the removal of sebum and residue. Negative charge of the hair fiber repels the also negative charge of the micelle. The repulsion of charges allows rinsing with water. However, the result is an increase of the preexisting negativity of the strands and the formation of stable complexes that bond with the keratin, creating repulsion between the strands due to excessive static electricity. Although the cationic agents try to neutralize this effect, there is the interference of the shampoo pH, which can increase the static electricity and reduce charge neutralization. ^{[4]:[5]:[6]:[12]:[14]:[15]:[16]}

Anionic surfactants

Anionic surfactants are characterized by a negatively-charged hydrophilic polar group. Examples of anionic surfactants are ammonium lauryl sulfate, sodium laureth sulfate, sodium lauryl sarcosinate, sodium myreth sulfate, sodium pareth sulfate, sodium stearte, sodium lauryl sulfate, alpha-olefin sulfonate, ammonium laureth sulfate. Although very good in removing sebum and dirt, anionic surfactants are strong cleaners and may cause

an increase on electrical negative charges on the hair surface and increase frizz and friction. In order to minimize damage, other surfactants called secondary surfactants such as nonionic and amphoteric surfactants are added to the formulation. ^{[5],[11],[17],[18]}

Cationic surfactants

Cationic surfactants have a positively charged hydrophilic end. Typical examples are trimethylalkylammonium chlorides, and the chlorides or bromides of benzalkonium and alkylpyridinium ions. All are examples of quats, so named because they all contain a quaternary ammonium ion. They tend to neutralize the negatively charged net of the hair surface and minimize frizz. They are often used as shampoo's softeners. ^{[5],[11],[17],[18]}

Amphoteric surfactants

For the amphoteric surfactants, the charge of the hydrophilic part is controlled by the pH of the solution. This means that they can act as anionic surfactant in an alkaline solution or as a cationic surfactant in an acidic solution. They are very mild and have excellent dermatological properties. There are two types of amphoteric compounds: Alkyl iminopropionates and (amido) betaines. ^{[5],[11],[17],[18]}

Nonionic surfactants

Nonionic surfactants have no electric charge. They do not ionize in aqueous solutions because their hydrophilic group is of a nondissociable. Many long chain alcohols exhibit some surfactant properties. Prominent among these are the fatty alcohols, cetyl alcohol, stearyl alcohol, and cetostearyl alcohol (consisting predominantly of cetyl and stearyl alcohols), and oleyl alcohol. ^{[5],[6],[11],[17],[18],[19],[20]}

Conditioners



Conditioners are used to decrease friction, detangle the hair, minimize frizz and improve combability. Conditioners act by neutralizing the electrical negative charge of the hair fiber by adding positive charges and by lubricating the cuticle that reduces fiber hydrophilicity. They contain anti-static and lubricating substances that are divided into 5 main groups: Polymers, oils, waxes, hydrolyzed aminoacids and cationic molecules. ^[5] The most active and used conditioner agent is a silicone. There are different types of silicones with different deposition, adherence and wash out capacity which will lead to different performances of the conditioner. ^{[21],[22],[23]} The ideal conditioner is capable of restore the hydrophobicity of the fiber and neutralize the static electricity. Depending on the capacity of entering the fiber, the conditioner may reach the cuticle surface or the inner part of the cortex. Smaller molecules can reach the cortex. Larger ones act on the cuticle. Low molecular weight polypeptides (<10.000 Da) can diffuse into hair. Bigger molecules (500.000 Da) can diffuse into the cuticle, especially on bleached hair. The preferred route is intercellular diffusion or diffusion through the nonkeratin regions, although intracellular diffusion may also occur. Higher molecule weight polymers (<600.000 Da) may sorption on the surface of the hair shaft. ^[5] Cationic ingredients such as cationic polymers are very popular in hair products. They can be so substantive to the hair that they can be difficult to remove. They are highly substantive to hair because of the hair's low isoelectric point (pH - 3.67). Any cosmetic with higher pH bears a net negative charge on the hair surface, and therefore cationic charges (positive) are attracted to it. Also, Van der Waals forces and entropy are necessary to bind the molecule to the fiber, and they must be resistant to rinsing with water. ^{[5],[22]} Examples of such polymers are: Benzyl dimethyl ammonium chloride and distearyldimonium chloride. The good correlation between silicone oil droplets stability, deposition on hair and resultant friction of hair support that droplet size and uniformity are important factors for controlling the stability and deposition property of emulsion based products such as shampoo and conditioner. ^[20]

It is common to use cationic ingredients in many shampoos' formulations with anionic surfactants in order to result in charge neutralization forming a cationic-anionic complex, a neutral hydrophobic ingredient. Therefore, we can understand that the interaction between the ingredients is more important than the ingredient alone, as we are led to believe by the media. It is very common to think that a new release product that contains a certain ingredient has the magic ability to transform dull hair into shiny and smooth hair. Most of the time, the major ingredients do not change, and sometimes the capacity of the ingredients to interact inside the shampoo's or conditioner's chassis or system is what makes the product acts better. Bleached and chemical treated hair have

a higher affinity to conditioning ingredients because they have a low isoelectric point (higher concentration of negative sites) and are more porous than virgin hair.